

The ABCs of PFCs in Water Supplies

By Christina Alito, PE, PhD, ENV SP – Water/Wastewater Engineer, Vienna, VA,
and Pierre Kwan, PE – Senior Project Manager, Seattle, WA



PFCs are present at increased concentrations in source waters and have public health implications

What are perfluorinated compounds and why are they a concern?

Perfluorinated compounds (PFCs) are a persistent group of manufactured organofluorine chemicals that have served many purposes in industrial and consumer product applications. Also referred to as perfluorinated alkyl substances (PFASs), PFCs have been utilized for their ability to repel oil and water and long-term stability. Several compounds are categorized as PFCs, including perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS)

(Figure 1). These two compounds are the primary concern to drinking water utilities and regulators since they are present at increased concentrations in source waters and have public health implications.

PFCs are very stable in the environment. Not only are they slow to degrade, but they can form degradation by-products that also present toxicity concerns. Their presence has been measured in water, soil, air, food and even human blood. The half-life of PFCs in the human body can range from four months to

over nine years. Increased exposure to high concentrations of PFCs has been shown to cause negative health effects in laboratory animals, such as abnormal endocrine activity, tumors, organ damage, reduced immune system function and reproductive and developmental problems.

PFCs can be clustered into two primary groups: "long-chained" and "short-chained" (Figure 2). Long-chain PFCs typically are designated as perfluoroalkyl sulfonic acids (PFSAs) containing six or more carbons and perfluoroalkyl carboxylic acids (PFCAs) containing eight or more carbons. Short-chain PFCs, which have fewer than six carbon molecules, can be degradation by-products of long-chain PFCs or independent compounds. Since degradation of long-chained PFCs is more challenging, they tend to persist in aquatic environments longer than short-chained PFCs. Conversely, short-chain PFCs can be more difficult to remove by treatment methods, like activated carbon, due to their limited capacity for adsorption.

Regulation of PFCs

Presently, there are no enforceable federal drinking water limits for PFCs or any degradation products. As the negative health effects of PFCs became more apparent in the early 2000s, the United States Environmental Protection Agency (EPA) began to provide PFC concentration guidelines through provisional health advisories for PFOA and PFOS. In an effort to phase out usage of PFCs, EPA's 2010/2015 PFOA Stewardship Program coordinated emissions reduction of PFCs with eight large chemical companies. Under this program, companies aimed to reduce 95 percent of PFOA and long-chained PFCs by 2010 and completely eliminate emission of long-chained PFCs by the end of 2015.

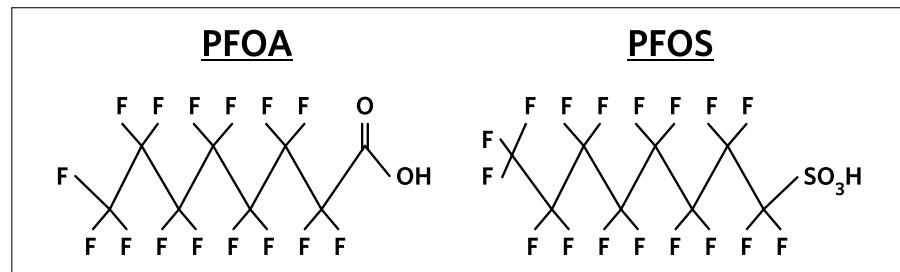


Figure 1: Chemical structure of PFOA and PFOS

		LONG-CHAINED	SHORT-CHAINED
	Nonstick Cookware	Perfluorooctanoic Acid (PFOA)	N/A
	Fabric Protection	Perfluorooctane Sulfonate (PFOS)	Perfluorobutanesulfonic Acid (PFBS)
	Aqueous Film Forming Foam (Firefighting)	Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoic Acid (PFOA)	Perfluorohexane Sulfonic Acid (PFHXS)
	Food Containers - Plastic Surfactants	Perfluorononanoic Acid (PFNA)	N/A

Figure 2: Primary PFCs identified in drinking water and industrial sources

Independent studies conducted by the Department of Defense identified PFCs as a group of emerging contaminants because they have accessible pathways to enter the environment, pose a human health or environmental risk and do not have regulatory standards based on peer-reviewed research.

In May 2016, the EPA released drinking water lifetime health advisories (LHAs) for PFOA and PFOS that are based on adverse reproductive and developmental health effects. The new LHAs recommend that PFOS and PFOA concentrations, individually or combined, be limited to

0.070 micrograms per liter ($\mu\text{g}/\text{L}$) to prevent potential public health impacts. In addition to the federal PFC LHAs, individual states have begun to adopt their own monitoring guidelines. Vermont, Maine, Illinois, Michigan, Texas, North Carolina, Minnesota, New Jersey, Nebraska, Pennsylvania and Washington have all developed guideline concentrations for PFCs in different water matrices. Some state guidelines focus primarily on groundwater remediation objectives, such as North Carolina (groundwater interim maximum allowable concentration of PFOA = $2 \mu\text{g}/\text{L}$), while other states have focused on drinking water concentration

guidelines, like New Jersey (preliminary drinking water guidance level of PFOA = $0.04 \mu\text{g}/\text{L}$). The New Jersey Drinking Water Quality Institute recently proposed a PFOA Maximum Contaminant Level (MCL) of $0.014 \mu\text{g}/\text{L}$.

Presence of PFCs in Drinking Water Supplies

PFCs are very soluble in aquatic systems, making them difficult to remove from various water sources. The chemical nature of PFCs makes biodegradation, photolysis and hydrolysis more challenging. PFCs can partition into water from various sources, such as consumer products, indoor and outdoor air, food packaging and other points of origin. The use of firefighting foams and industrial discharges typically provides the highest point source concentrations of PFCs in source waters. It is also possible for PFCs to enter drinking water sources such as groundwater or surface waters through wastewater effluent and application of biosolids, landfill leachate and stormwater runoff streams.

In the United States, PFCs have been identified in source water in the $\mu\text{g}/\text{L}$ level or lower and finished water locations at the nanogram per liter (ng/L) level. Data collected as part of the EPA's Unregulated Contaminant Monitoring Rule 3 (UCMR 3) provides the most comprehensive assessment of PFCs' presence in public water systems (PWSs). Results from sampling at 4,864 PWSs showed 0.9 percent of PWSs exceed the LHAs for PFOA and 0.3 percent of PWSs exceed the LHAs for PFOS. Other measured PFCs were below detection limits.

Treatment Options for Removal of PFCs

The removal efficiency of treatment techniques for PFCs from source waters depends on influent water characteristics including the total PFC concentration and the treatment method utilized. While conventional treatment methods have proven to be unsuccessful for PFC removal, advanced treatment techniques can reduce PFC concentrations by 90 percent or higher. Figure 4 shows PFC removal rates for advanced treatment methods.

STATE	MATRIX	CONTAMINANT
ILLINOIS	Groundwater	PFOA - $0.4 \mu\text{g}/\text{L}$ PFOS - $0.2 \mu\text{g}/\text{L}$
MAINE	Groundwater	PFOA - $0.06 \mu\text{g}/\text{L}$ PFOS - $0.1 \mu\text{g}/\text{L}$
MICHIGAN	Surface Water	PFOA - $0.42 \mu\text{g}/\text{L}$ PFOS - $0.012 \mu\text{g}/\text{L}$
MINNESOTA	Drinking Water + Fish Consumption	PFOA - $0.61 \mu\text{g}/\text{L}$ (Lake) PFOA - $0.72 \mu\text{g}/\text{L}$ (River) PFOS - $0.012 \mu\text{g}/\text{L}$ (Lake) PFOS - $0.006 \mu\text{g}/\text{L}$ (River)
NEW JERSEY	Drinking Water	PFOA - $0.04 \mu\text{g}/\text{L}$
NORTH CAROLINA	Groundwater	PFOA - $2.0 \mu\text{g}/\text{L}$

Figure 3: State PFC concentration guidelines

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ACTIVATED CARBON FILTRATION

Granular activated carbon (GAC) and powdered activated carbon (PAC) are used for removal of PFCs from source waters. GAC filtration is a highly effective and commonly used treatment method for persistent long-chained PFC removal with greater than 90 percent removal of perfluororonanoic acid (PFNA), PFOA and PFOS. Process optimization may be necessary to ensure that pH, temperature, empty bed contact time and other water quality factors are optimal for effective removal of PFCs. The usage of GAC also requires maintenance to establish efficient carbon usage rate, disposal or regeneration of GAC as needed.

PAC is another form of activated carbon with smaller diameter particles that can be added to as a pretreatment step at a water treatment plant. Higher concentrations of PAC may be necessary to reach the same removal rates as GAC, which can increase the costs for treating PFCs.

ANION EXCHANGE

Anion exchange utilizes a special ion exchange material (usually commercial resins or petrochemical compounds) shaped as beads to exchange anions in untreated water and replace them with hydrogen or hydroxyl ions. The rate of exchange will depend on many factors, including influent PFC concentration, design of the anion exchange system and bead material. While anion exchange has shown varying degrees of effectiveness in removing PFCs, porous anion exchange resin impregnated with iron oxide has been shown to remove up to 90 percent of some PFCs from drinking water.

HIGH-PRESSURE MEMBRANE FILTRATION

Reverse osmosis (RO) and nanofiltration (NF) are both effective methods for removing PFCs from drinking water. RO uses a semi-permeable membrane to allow osmotic pressure to retain PFCs on the pressurized side of the membrane while the purified water passes through it. RO works most efficiently when influent water is pretreated to prevent membrane fouling and has been shown to achieve up to 99 percent removal of PFOS and PFOA from drinking water.

TREATMENT METHOD	TARGET PFC REMOVAL RATE
GRANULAR ACTIVATED CARBON	PFOA = 90 percent or greater PFOS = 90 percent or greater
ANION EXCHANGE	PFOA = 10-90 percent PFOS = 90 percent or greater
HIGH-PRESSURE MEMBRANE FILTRATION	PFOA = 90 percent or greater PFOS = 90 percent or greater
ADVANCED OXIDATION	PFOA = less than 10 percent PFOS = 10 to 50 percent
DISSOLVED AIR FLOTATION	PFOA = less than 10 percent PFOS = up to 50 percent

Figure 4: PFC treatment method efficiency

NF uses filters with pore sizes around 0.001 micron with a high water flux to remove most contaminants, including organic molecules, viruses and salts. NF has been shown to remove up to 90 percent of PFOS and PFOA from drinking water. Rejected water from RO/NF should be contained properly to reduce contamination of nearby waters from PFCs and other pollutants.

ADVANCED OXIDATION

Advanced oxidation processes (AOP) utilize strong oxidants such as UV/H₂O₂,

Fenton, UV/S₂O₈²⁻ (persulfate) and Fe²⁺/UV to destroy recalcitrant organic compounds through the production of hydroxyl radicals. The effectiveness of AOP treatment on organic compounds is greatly dependent on the water quality of the treated water and the minimization of interference compounds. Although research is still ongoing, preliminary results have shown that AOP can effectively remove 10 to 50 percent of PFOS and less than 10 percent of PFOA from drinking water sources.



Granular activated carbon (GAC) treatment system for PFC removal, City of Issaquah, Washington

DISSOLVED AIR FLOTATION

Dissolved air flotation (DAF) systems utilize micro air bubbles from diffuser nozzles to attach and float flocculated solids from influent water to the top of the DAF basin. Once the suspended matter has reached the top of the basin, the floating material is skimmed off or removed through a desludging trough while clarified water flows out of the bottom of the chamber. Preliminary studies have shown up to 50 percent potential for removal of long-chained PFCs like PFOS and PFNA.

Case Study - Issaquah, Washington

Issaquah, Washington, is a Seattle-area suburb that provides drinking water to its customers using a combination of its four groundwater wells and purchased regional surface water supplies. As part of EPA's UCMR 3, the City detected PFCs in its 250 gallon per minute (gpm) Well No. 4 supply, the primary compound being PFOS. PFOS concentrations were detected at 0.472 µg/L to 0.600 µg/L in the sampling. PFOA was also detected at a level of 0.018 µg/L. In response to the PFC detections, the City shut down Well No. 4 along with the adjacent, uncontaminated 1,150 gpm Well No. 5. The Well No. 4 aquifer is above the Well No. 5 aquifer, and Well No. 5 was shut down to avoid downward PFC migration to the more productive Well No. 5 aquifer.

With the summer season quickly approaching, the City of Issaquah sought an expedited solution that would allow them to meet customer peak water demands. The City engaged HDR professionals to quickly evaluate a number of temporary and long-term treatment alternatives to eliminate the PFC contamination from Well No. 4 so Well Nos. 4 and 5 could both be returned to operation before water demands increased. For various financial, operational and water quality reasons, expanded use of purchased regional supply water was not a viable option so the City concentrated on how to return the wells to service.

As a result, we worked very closely with City and State regulators to quickly design, permit and assist construction and startup of a treatment system to successfully remove PFC contamination from Well No. 4. Features were installed so that the

treatment system could be expanded to include Well No. 5 if that (lower) aquifer ever became contaminated. The installed treatment system consists of two pressure filters operated in series, each filled with 20,000 pounds of GAC. The time between City Council authorization and sending GAC-treated water to distribution was only 77 days. The treatment system has successfully reduced PFOS and PFOA concentrations to non-detectable levels in all treated water samples since its start in June 2016.

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For more information about this article, please contact Christina Alito, Christina.Alito@hdrinc.com, or Pierre Kwan, Pierre.Kwan@hdrinc.com